# Appendix 4A-7: Technical Analysis Supporting a Request for Modification/Variance from STA-2 Mercury Startup Criteria

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#### **SUMMARY**

Cells 2 and 3 of Stormwater Treatment Area 2 (STA-2) have met their mercury startup criteria, but Cell 1 still had not as of May 1, 2001. In addition, just prior to dryout the anomalous buildup of mercury in Cell-1 fish continued. This could represent an unacceptable risk to sensitive members of some fish-eating wildlife species foraging in the cell preferentially. Following reflooding, with a mixture of canal water and rainwater under wet-season conditions, this mercury anomaly is likely to recur and Cell 1 is again unlikely to meet its mercury startup criteria. The South Florida Water Management District (District) has concluded this is a consequence of Everglades-like biogeochemical conditions occurring in Cell 1 and that these conditions are presently outside the District's control. The District has further concluded that an extended period of standing water in STA-2, Cell 1 is likely to be the worst case for methylmercury production, bioaccumulation and risk.

The District is requesting a modification of, or variance from, the mercury startup condition in the Everglades Forever Act (EFA) permit for STA-2 to allow startup of Cell 1 flow-through operation now. This will prevent an extended period of standing water and substantially reduce the likelihood of methylmercury buildup to anomalously high levels in water, soil and aquatic biota. The purpose of this report is to support this permit modification or variance request using technical information available on mercury sources, transport, storage, transformation and effects in the Everglades and elsewhere. Having the flexibility to initiate flow-through operation now during high-flow events will also result in a greater reduction in the phosphorus load entering the Northern Everglades than if only Cells 2 and 3 were operational. It is also likely to produce a substantial decrease in the mercury concentrations of Cell 1 water and fish without a concomitant substantial increase in mercury concentrations in downstream fish.

The District has determined that an average depth of one foot (0.3 m), with a minimum depth of 6 inches (0.15 m), could foster the buildup of sulfide concentrations in pore water to levels that will inhibit methylmercury production, as long as the soil and water chemistry conditions are otherwise conducive. To ensure sufficient water is available to maintain the required average and minimum water depths in STA-2, Cell 1, once it is determined that STA-2, Cell 1 capacity will be required to treat all of the water from a high-flow event, flow allocation priority will be given to STA-2, Cell 1 over Cells 2 and 3. Despite these precautions, if methylmercury concentrations in

fish rise to levels that potentially threaten public health or endangered or migratory species, STA-2, Cell 1 can be dried out, diluting the excess methylmercury in Cell 2 and 3 discharges. In this way any unanticipated methylmercury trajectory within STA-2, Cell 1 can be accommodated.

#### INTRODUCTION

Cells 2 and 3 of Stormwater Treatment Area 2 (STA-2) have met the mercury startup criteria set forth in the state's Everglades Forever Act permit (No. 012764), but Cell 1 still has not. As of this writing. Cell 1 has dried out as a consequence of the unprecedented drought conditions in South Florida. Based on past experience (Krabbenhoft and Fink, 2001; Krabbenhoft et al., 2000) and best available information, it can be predicted with high confidence that subsequent reflooding of Cell 1, when water becomes available, will reinitiate an anomalous methylmercury event. Following reflooding, it can be projected with high confidence that the "first-flush" methylmercury pulse will propagate up the food chain through all trophic levels (Cleckner et al., 1998; Hurley et al., 1998; Lange et al., 1998; Loftus et al., 1998). It can be further projected with moderate confidence that this anomalous condition will persist under wet-season conditions until sulfide concentrations can build up to inhibitory levels in surficial peat soil pore water, reducing the rate of methylmercury production (Craig and Bartlett, 1978; Compeau and Bartha, 1984; Gilmour et al., 1998a,b; Benoit et al., 1999a,b; Jay et al., 2000; Benoit et al., 2001; Marvin-DiPasquale et al., 2001). This is only likely to occur when flow-through operation is initiated, increasing the sulfate loading rate to STA-2, Cell 1 under conditions favorable to sulfide production. Flowthrough operation can be initiated only if the mercury startup criteria can be met, but under the present circumstances and conditions it is unlikely this will happen. This biogeochemical dilemma constitutes the compelling need for a permit modification or variance that will allow the District to initiate flow-through operation now.

The purpose of this report is to support the District's request for the required permit modification or variance. To fulfill this purpose, the report first provides basic background information, then summarizes the anticipated methylmercury impacts and their likely causes within and downstream of STA-2, Cell 1 from initiation of flow-through operation. The next section focuses on the likely future methylmercury trajectories and risk consequences under three operational scenarios: (1) initiating flow-through operations in Cells 2 and 3 only, with standing water in Cell 1; (2) same as (1), but with Cell 1 completely dried out; and (3) flow-through operation of all three cells. More detailed background information and a detailed analysis of the data collected in the STA-2 expanded mercury study are contained in the "Report on Expanded Mercury Monitoring at STA-2," which is **Appendix 4A-6** of the 2002 Everglades Consolidated Report.

#### **BACKGROUND**

#### STA-2

STA-2 is a constructed wetland permitted for the removal of total phosphorus in farm runoff and Lake Okeechobee releases. It consists of three treatment cells that can be operated independently. Cells 2 and 3 are 2,220 acres each, while Cell 1 is 1,990 acres. When fully operational, STA-2 will receive an average of 174,641 acre-ft (21,540,000,000 cubic meters) per year of untreated stormwater runoff and Lake Okeechobee releases from the S-6 Pump Station (District Contractor Report, 1996) and will discharge treated water into the L-6 Canal, and thence through control structures, into the northwestern quadrant of Water Conservation Area 2A (WCA-2A). More detailed background information is contained in **Appendix 4A-6**.

The works required to initiate flow-through operation of STA-2 are likely to be completed in the next two months, and the District would like to be able to initiate flow-through operation of STA-2 as soon thereafter as possible to maximize the benefit of total phosphorus removal from farm runoff and Lake Okeechobee releases to the Everglades.

The state permit issued by the Florida Department of Environmental Protection (FDEP or Department) to the District for operation of STA-2 (EFA 0126704; NPDES FL0177946) precludes initiation of flow-through operation of a treatment cell until the total phosphorus concentration at the outflow is less than the inflow, and the total mercury and methylmercury concentrations in the interior are not significantly greater than the inflow. NPDES Permit No. FL0177946 incorporates these EFA permit conditions by reference. STA-2, Cells 1, 2 and 3, met startup requirements for total phosphorus on September 13, 2000, Cells 2 and 3, met startup requirements for mercury on September 14 and November 9, 2000, respectively, but Cell 1 still has not as of the last sampling event prior to dryout in mid-April 2001.

#### THE ANOMALOUS MERCURY EVENT IN STA-2 CELL 1

The EFA permit also requires reporting anomalous mercury conditions that develop during startup or subsequent routine operations. The benchmark for normal mercury conditions is the Everglades Nutrient Removal (ENR) Project (SFWMD, 1995 through 1999; Fink, 2000), the demonstration-scale STA that operated from Summer 1994 through Spring 1999, when it was incorporated into STA-1W. The average interior total mercury and methylmercury concentrations for the ENR Project were 1.1 ng/L and 0.11 ng/L, respectively (**Appendix 4A-6**). An anomalous methylmercury concentration of 4.8 ng/L was detected in the interior of STA-2, Cell 1 in a September 26, 2000 collection and was reported to FDEP on October 13, 2000 following quality assurance confirmation.

Methylmercury is a highly toxic (Clarkson, 1994) and bioaccumulative (Norstrom et al., 1976; Rodgers, 1994; Lange et al., 1998; 1999) organic form of mercury produced primarily by sulfate-reducing bacteria (SRB) of the genus *Desulfovibrio* living primarily in the top four cm of surficial sediment or hydrated peat soil (Gilmour et al., 1998a,b). This transformation is carried out in the presence of an oxidized form of sulfur, sulfate and short-chain carboxyllic acids, but in the absence of dissolved oxygen (Wood et al., 1968; Jensen and Jernelov, 1969; Olson and Cooper, 1976; Compeau and Bartha, 1984; Gilmour and Henry, 1991; Gilmour et al., 1992; Gilmour et al., 1998a,b; Krabbenhoft et al., 2000; Marvin-DiPasquale, 2001). However, methylmercury

production has also been measured in periphyton mats (Cleckner et al., 1999) and the roots of floating macrophytes (Mauro and Guimaraes, 1999; Hurley et al., 1999).

At FDEP's request, the District initiated a 90-day expanded mercury monitoring program in Cells 1 and 2 to more fully characterize the methylmercury conditions in Cell 1, to identify known or potential causes of the very different startup trajectories of Cells 1 and 2 and to evaluate options for mitigation should such become necessary. The results verified the results for water while detecting anomalously high concentrations of methylmercury in sediment and mosquitofish (**Appendix 4A-6**). As of the March 2001 collection, the average total mercury concentration in Cell-1 mosquitofish exceeded that at WCA-3A-15, the Everglades "hot spot," and there was no evidence a plateau had yet been reached (**Appendix 4A-6**). By analogy to similar systems, anomalously high concentrations of methylmercury can also be inferred to be building up in fish species at the next trophic level, including sunfish species, which are typically consumed by fisheating wildlife (Rumbold et al., 2000a; 2001).

An immediate, acute toxic threat to fish-eating wildlife feeding exclusively in STA-2, Cell 1 is highly unlikely; however, there is a likelihood of chronic toxic effects from long-term methylmercury exposure to highly exposed, highly sensitive members of fish-eating wildlife populations foraging preferentially in STA-2 Cell 1 (Rumbold et al., 2000b; **Appendix 4A-6**). Populations at risk include wading birds roosting or nesting in the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), but foraging over a range that includes STA-2. Just prior to the dryout of Cell 1 in April 2001, the water-column concentration of unfiltered methylmercury again rose to an anomalously high level (4.2 ng/L). However, with the dryout of Cell 1 in mid-April 2001, direct exposure to fish-eating wildlife has been interrupted (**Appendix 4A-6**).

## FACTORS CONTROLLING METHYLMERCURY PRODUCTION AND BIOACCUMULATION IN AND DOWNSTREAM OF CONSTRUCTED WETLANDS IN THE EVERGLADES

Methylmercury in the Everglades is produced from inorganic mercury present in wet and dry atmospheric deposition, surface flow and peat soils and, absent a dryout or burn event (Gilmour et al., 1991; Krabbenhoft et al., 2000; Krabbenhoft and Fink, 2001), the relative contributions of each change in a predictable and gradual way with location and time of year (Fink and Rawlik, 2000). It is a virtual certainty that wet and dry atmospheric deposition to Cells 1, 2 and 3 were roughly equal during startup (Guentzel, 1997; Fink and Rawlik, 2000; Rumbold et al., 2000, 2001; Guentzel et al., 2001), so the significant differences in the methylmercury concentrations in soil, water and mosquitofish between cells must be attributed to some other factor or factors, such as antecedent land use, antecedent stage duration without and with dryout, differences in the hydraulic loading rates of makeup water or intrinsic differences in soil chemistry. Based on topographic considerations, Cell 1, with the highest elevation, is likely to dry out first, followed by Cell 2 and then Cell 3. To the extent that frequent dryout and rewetting accelerate methylmercury production, one might expect Cell 1 to behave anomalously. Due to the dryout of Cell 1 and the apparently imminent dryout of Cells 2 and 3, the remainder of this section focuses on the effect of dryout and reflooding on methylmercury production and bioaccumulation, taking into account the effect of differences in soil chemistries attributable to differences in antecedent land use.

Following soil dryout it can be confidently predicted that carbon, sulfur and iron species in surficial soils are oxidized, albeit to different degrees and at different rates (Dmitriw et al., 1995; Yin et al., 1997; Lamers et al., 1998; Gun et al., 2000; Taillfert et al., 2000; W. Orem, USGS, personal communication, 2000; Fink, 2001). Reinundation of oxidized soils is usually accompa-

nied by a "first-flush" release of nutrients (Newman and Pietro, 2000) and trace metals, including inorganic mercury (Dmytrw et al., 1995; Rawlik, 2001a,b). Following the first-flush release of inorganic mercury, some of it is either converted to dissolved elemental mercury, Hg(0), and then lost to the overlying air via evasion (Vandal et al., 1994; Saouter et al., 1995; Krabbenhoft et al., 1998; Lindberg and Zhang, 2000; Zhang and Lindberg, 2000) or it is reabsorbed by bacteria microfilms (Hintelman et al., 1993), algae (Hurley et al., 1998; Miles and Moye, 2000) and floating and rooted macrophytes (SFWMD, 1995-1999; Hurley et al., 1998; Fink and Rawlik, 2000), as well as the surficial peat soil (Ambrose and Araujo, 1998). Thereafter, it has been hypothesized that the presence of high concentrations of these oxidized species in a readily bioavailable form accelerates methylmercury production until they are reduced by biotic or abiotic processes (Krabbenhoft and Fink, 2000; Krabbenhoft et al., 2000). Following the production of this methylmercury pulse, it absorbs in a similar fashion to inorganic mercury (see above discussion), is decomposed to inorganic mercury or elemental mercury by sunlight (Sellers et al., 1996; Krabbenhoft et al., 1998; D. Krabbenhoft, USGS, personal communication, 2000), or is demethylated by carbonoxidizing and sulfate-reducing bacteria under anaerobic conditions (Oremland et al., 1991; Marvin-DiPasquale and Oremland, 1998; Pak and Bartha, 1998; Marvin-DiPasquale et al., 2000; Marvin-DiPasquale et al., 2001)

If the duration of accelerated methylmercury production is short because the soil pools of labile, bioavailable sulfate, carbon and inorganic mercury are small and rapidly consumed, then the total mass of methylmercury produced will be small and the magnitude and duration of subsequent excessive bioaccumulation of methylmercury in top predator fish and their predators will be short lived. This is the so-called "first flush effect." Conversely, if these pools are large, or there is an external source of the limiting factor capable of sustaining a high, first-flush methylmercury production rate for a long time, then the first-flush mass of methylmercury produced will be large. It will then result in excessive bioaccumulation at the top of the food chain and it will clear slowly from the ecosystem. This results in the so-called "reservoir effect," first observed in hydroelectric reservoirs created by flooding forested glacial till soils in northern temperate regions (Bodaly et al., 1984; Scruton et al., 1994; Rodgers et al., 1995), but is also observed in natural, created or expanded wetlands (St. Louis et al., 1994; St. Louis et al., 1996; Kelly et al., 1997; Paterson et al., 1998). This has also resulted in the increase in methylmercury body burdens in insect-eating birds (Gerrard and St. Louis, 2001) and fish-eating birds and mammals foraging in these water bodies (Wolfe et al., 1994).

However, if labile, bioavailable sulfate is present in substantial excess, surficial sediments remain anaerobic and no other factor limits microbial metabolism or affects sulfur speciation, then sulfide, a byproduct of the life processes of sulfate-reducing bacteria, can accumulate to concentrations that actually inhibit methylmercury production (Craig and Bartlett, 1978; Compeau and Bartha, 1984; Berman and Bartha, 1986; Gilmour et al., 1998b; Benoit, 1999a,b; Jay et al., 2000; Benoit et al., 2001; Marvin-DiPasquale et al., 2001). It has been hypothesized with moderate confidence (Gilmour et al., 1998b) that sulfide inhibition is causing eutrophic Everglades regions with conditions otherwise deemed ideal for methylmercury production (e.g., ENR Project and WCA-2A-F1) to exhibit low methylmercury production and correspondingly low concentrations in fish at all trophic levels (Cleckner et al., 1998; Lange et al., 1998; 1999; Loftus et al., 1998; Rumbold et al., 2000; Rawlik, 2001a; Rumbold et al., 2001). Conversely, unimpacted or virtually pristine areas in the Everglades exhibit much higher methylmercury production rates (e.g., WCA-2A-U3 and WCA-3A-15) and correspondingly higher concentrations in fish at all trophic levels.

Results of a joint USGS-District study of an Everglades dryout and burn that occurred in spring 1999 suggest that the relatively rapid decline from peak methylmercury concentrations in

pore water and soils was brought about by the rapid depletion of the excess sulfate pool created by the oxidation of inorganic and organic sulfides; however, the alternative hypothesis that this was caused by the relatively rapid onset of sulfide inhibition cannot be ruled out (Krabbenhoft and Fink, 2000; Krabbenhoft et al., 2000). The relatively rapid onset of sulfide inhibition in sulfur-amended agricultural soils could also explain why STA-1W Cell 5, after exhibiting a first-flush effect, relaxed back to ENR-like conditions within 180 days of startup.

### THE ANTICIPATED MERCURY IMPACTS OF FLOW-THROUGH OPERATION

This section addresses the anticipated impacts of initiating flow-through operation on methylmercury production and bioaccumulation within STA-2 Cell 1 and the already impacted areas in WCA-2A to which the treated discharge will be directed. The focus is on the influence of the excess sulfate in canal water on methylmercury production and bioaccumulation within and downstream of STA-2, but the influence of inorganic mercury loads, flow dilution and phosphorus-mediated biodilution are also discussed. Unless otherwise stated, all correlation analyses were carried out using the Microsoft Excel spreadsheet program packaged with Microsoft Office SR-97 running on a Windows 95 platform.

#### STA-2 Cell 1

#### **METHYLMERCURY PRODUCTION**

The soil methylmercury production rate in the top four cm of peat soil is believed to the primary determinant of the concentration of methylmercury in water, soils and aquatic biota (Gilmour et al., 1998a,b), but methylmercury production rates cannot be measured directly in situ. A number of measurements have been made on intact soil cores (Gilmour et al., 1998a,b; Marvin-DiPasquale, 2001; D. Krabbenhoft, USGS-Madison, personal communication, 2001). Where methylmercury production rates in intact soil cores are high, the concentration of methylmercury in soil solids tends to be high, so in the absence of direct measurements of the *in situ* methylmercury production rate the concentration of methylmercury in soils can be used as a surrogate for the methylmercury production rate (Gilmour et al., 1998a). The concentration of methylmercury in the top four cm of Everglades soils is most strongly inversely correlated with the concentration of sulfide in pore water (r = -0.45; log transformed r = -0.78) and the chromate reducible sulfide (CRS) fraction of soil solids (r = -0.38; log transformed r = -0.64), but less so with total mercury in pore water (r = -0.28; log transformed r = -0.37) or soil solids (r = 0.17; log transformed r = -0.38) 0.20) (District calculations based on data supplied by C. Gilmour, ANSERC, 1999). When the linear correlation analysis is carried out on the historical average pore water and solids chemistry values (top five cm) at nine sites in the period 1995 through 1998 (calculated from data supplied by USGS with Krabbenhoft et al., 2000), the inverse correlation between MeHg in surficial soil and pore water sulfide increases (r = -0.72; log transformed r = -0.85), as does that with total mercury in soil solids (r = 0.66; log transformed = 0.46). An inverse relationship between soil sulfide and methylmercury production rate might be expected because of the high affinity of reduced sulfur species in soil humic substances for inorganic mercury (Xia et al., 1999), but it is more likely this is due to the effect of soil and pore water sulfide on inorganic mercury speciation (Benoit et al., 1999a,b; Jay et al., 2000; Benoit et al., 2001). The addition of ferrous sulfide slurry to a homogenized Everglades sediment has also been demonstrated to reduce net methylmercury production (Marvin-DiPasquale et al., 2001).

#### INORGANIC MERCURY LOAD

The external inorganic mercury load to Cell 1 from S-6 canal water and wet and dry atmospheric deposition will be approximately the same as those to Cells 2 and 3. In addition, the concentration of inorganic mercury in Cell 1 soils is not significantly different than the concentrations in Cells 2 or 3 (**Appendix 4A-6**). However, based on its anomalous response to reflooding following dryout, it is likely the inorganic mercury released during the second first-flush event will be eventually redeposited in the surficial soil. This may explain why the total mercury in the top four cm of homogenized soils in Cell 1, collected in December 2000, was higher than that in the homogenized 10-cm core collected in April 1999. If this redeposition precedes the onset of sulfide inhibition or sulfide inhibition never occurs, the sulfate-reducing bacteria living in this layer of redeposited inorganic mercury will likely stimulate the production of methylmercury at a higher rate than would have occurred without dryout and reflooding. This may explain why the total mercury (as a surrogate for methylmercury) concentrations in Cell 1 mosquitofish continued to climb many months after the presence of the first-flush fluxes of inorganic mercury and methylmercury were no longer detectable in surface water (**Appendix 4A-6**).

#### SULFATE LOAD

The strong inverse relationship between soil methylmercury and pore water sulfide discussed above suggests it should be possible to predict post-flow-through soil and mosquitofish methylmercury concentrations from post-flow-through soil pore water sulfide with the required accuracy and confidence level. It is also reasonable to expect that a direct mechanistic relationship exists between surface water sulfate and soil pore water sulfate and between pore water sulfate and pore water sulfide, and that these intuitively obvious mechanistic relationships will be reflected in strong empirical relationships. This approach to predicting post-flow-through methylmercury production and bioaccumulation is especially attractive, because a review of the surface water quality data for the period 1995 through 2000 indicates that the average sulfate concentration at the ENR Project inflow (63.5 mg/L; SFWMD 1995-1999; unpublished District data, 2000) is virtually indistinguishable from that at S-6 (64.8 mg/L), which is the inflow water source for STA-2 upon initiation of flow-through operation (Bechtel et al., 1999; Chapter 2, 2001 Everglades Consolidated Report; unpublished District data, 2001). The compounding of empirical relationships to carry out the desired predictions will propagate substantial uncertainty into the final result, so any management decision based on the predictions obtained with this approach would require offsetting margins of safety.

The uncertainties in this sequential empirical approach notwithstanding, to determine whether the prediction of pore water sulfide from surface water sulfate was possible, a review was undertaken of the extant Everglades data sets where surface water and pore water chemistry data could be paired spatially and temporally. Data sets meeting these criteria were obtained from the District's ENR Project and the WCA-2A "F" transect studies. In addition, the USGS Aquatic Cycling of Mercury in the Everglades (ACME) Study provided historical average surface and soil pore water concentrations of filtered total mercury, methylmercury and a limited number of influential chemical constituents (e.g., sulfate, DOC) at nine sites with the post-burn study data (Krabbenhoft et al., 2000), but the individual data from which the historical averages were calculated were unavailable as of this writing. Finally, District or ACME surface water data could be paired with individual soil solids and pore water chemistry data generated by the Academy of Natural Sciences Environmental Research Center for 4-cm cores collected at the same sites and times.

For the ENR Project, an inverse relationship was observed between surface and pore water sulfate (r = -0.79) in one set of paired surface and pore water data collected in January 1995 (District calculations based on unpublished District data), and a weak inverse relationship was observed between pore water sulfate and pore water sulfide (r = -0.12) for a limited set of ENR

Project data collected by ANSERC in the period 1995 through 1998 (District calculations based on data supplied by C. Gilmour, ANSERC, 1999). By comparison, paired surface water and pore water chemistry data collected quarterly along the WCA-2A transect in the period 1995 through 2000 exhibited a weak positive linear correlation between surface and pore water sulfate (r = 0.31; log transformed r = 0.16), but a much stronger positive linear correlation was observed in ANSERC data between pore water sulfate and sulfide in the top 4 cm of peat soils across the Everglades for sites excluding the ENR Project (r = 0.31; log transformed r = 0.73). These results underscore our inability to predict pore water sulfide concentrations from surface water sulfate concentrations alone with the required accuracy and confidence level because the relationship between the concentrations of surface water sulfate, pore water sulfate and sulfide and total sulfur, sulfate and inorganic and organic sulfides in soil solids is complex and is influenced by antecedent land use and stage duration and a number of site-specific, spatially heterogeneous, temporally variable and seasonally dynamic factors.

#### OTHER SOIL FACTORS

Other soil factors affect sulfur speciation and thus mercury speciation. Such factors include the iron content of the soil solids and pore water (Gilmour, 1991; Gilmour et al., 1998a; Marvin-DiPasquale and Capone, 1998). An analysis of the District data for the six 4-cm cores collected in Cells 1 and 2 in December 2000 produced a moderate inverse correlation between the bulk density weighted-average methylmercury concentration and the corresponding soil total iron concentration (r = -0.69), but not with soil total sulfur concentration (r = 0.2). Therefore, there are too few data to draw any strong conclusions. Nevertheless, this observation would be consistent with that of Lockwood and Chen (1974) that inorganic mercury sorbs strongly to iron (III)-hydroxide complexes, as well as with the observation that methylmercury production is suppressed when adding a ferrous sulfide (iron pyrite) slurry to homogenized Everglades soils dosed with 203-Hg radioisotope under anoxic conditions (Marvin-DiPasquale et al., 2001). This is seemingly inconsistent with the observed stimulation of methylmercury production with the addition of ferric chloride to lake sediments (Howard, 1993; Gilmour et al., 1996) and to an intact Everglades core (Gilmour et al., 1998a) and the slight stimulation of methylmercury production by the addition of ferrous chloride (FeCl<sub>2</sub>) to a homogenized core from WCA-3A-15 (Marvin-DiPasquale et al., 2001). Until these inconsistencies are resolved we will be unable to predict the absolute and relative concentrations of the various sulfur species known to influence methylmercury production from known soil solids and pore water chemistries.

#### THE EFFECT OF WATER DEPTH

Maximum methylmercury production at the 10 Everglades sites studied by ANSERC occurs in the top 4 cm of peat soil under anaerobic conditions (Gilmour et al., 1998b). One might expect that deep water is associated with a lower average dissolved oxygen concentration in the water column and thus a correspondingly lower redox potential in the underlying surficial peat soil, and vice versa. Deep water and shallow water are also associated with less and more mixing of surface and pore water chemistries, with a breakpoint depth at about 10 cm (G. Aiken, USGS-Boulder, personal communication, 2001). All other factors being equal, deep water should foster a higher sulfate-reducing bacteria activity and a higher sulfide production rate than shallow water. Where sulfate is in excess, this would result in the eventual buildup of sulfide in pore water to levels inhibitory of methylmercury production. Conversely, in shallow water the buildup of sulfide to inhibitory levels would be less likely to occur. Two questions arise: (1) What is the relationship between water depth and the factors that can or will determine methylmercury production (e.g., surface water dissolved oxygen, pore water sulfide); and (2) What is the water depth below which inorganic and organic sulfide species are oxidized to sulfate, releasing the sulfide brake on methylmercury production?

To answer the first question, an analysis of paired surface water data, collected by McCormick and coworkers in the District's Everglades Research Department from the "F" transect along the WCA-2A nutrient gradient in the period 1995 through 2000, was carried out. The dissolved oxygen data were not standardized to a reference temperature. In addition, both surface and soil chemistries and aquatic ecologies are changing along the nutrient gradient, so all other factors are not equal. The preceding limitations notwithstanding, a weak inverse linear correlation was observed between dissolved oxygen and water depth at sites F1 (r = -0.31; n = 70), F2 (r = -0.31), F3 (r = -0.31), F4 (= -0.40; n = 86), F3 (r = -0.35; n = 81), and F4 (r = -0.28; n = 73) – the highly eutrophic sites – while a weak positive linear correlation was observed at site U3 (r = 0.36; n = 82), the oligotrophic site along the nutrient gradient. At the transition site, F5, the relationship between dissolved oxygen and water depth also showed a transition, with r = 0.02 (n = 80). This analysis may be confounded, however, by the interaction of trophic state, autotrophic species densities and production rates and the dissolved oxygen concentration. The most obvious, potentially confounding covariate is total phosphorus, the limiting nutrient in the Everglades. The trophic gradient between F1 and U3 is highly correlated with the surface water total phosphorus concentration (McCormick et al., 1999), but the observed correlations between dissolved oxygen and water column total phosphorus at these sites were exceedingly weak, varying from r = 0.05 at F1 (n = 70) to r = 0.018 at U3 (n = 82).

Surficial (depth = 0 to 5 cm) pore water sulfide concentrations measured in the period 1995 through 2000 by Sue Newman and coworkers in the District's Everglades Research Department were paired with surface water dissolved oxygen concentrations and water depths measured by Paul McCormick and coworkers from that same department at sites F1 through F5 and U3 (n = 102). A weak positive linear correlation was observed between water depth and pore water sulfide (r = 0.22), while a weak inverse linear correlation was observed with surface water dissolved oxygen (r = -0.16). These relationships are strengthened for some sites and weakened for others when sites are evaluated individually. Focusing on the water depth-sulfide relationship, for F1, r = 0.42 (n = 13), while for U3, r = 0.14 (n = 12). When the data pairs are transformed by taking the natural logarithm, both relationships improve considerably, but both are still weak-to-moderate. For F1, r = 0.52, while for U3, r = 0.36. Unfortunately, this approach could not be extended to include methylmercury in soil pore water and solids because the latter data were collected by Gilmour and coworkers at F1 and U3 only, and no corresponding surface water depth or dissolved oxygen measurements were made at the same time.

To answer the second question, the concentration of sulfide can be estimated from the corresponding overlying water depth from a simple linear regression relationship. The depth at which the average sulfide concentration in pore water is greater than the maximum required for the onset of sulfide inhibition should be considered the breakpoint depth above which sulfide buildup is likely to occur if conditions are otherwise conducive. From manipulations of intact sediment cores, Krabbenhoft et al. (2001) report that onset of inhibition of inorganic mercury methylation occurs in the concentration range 10 to 100 micromolar inorganic sulfide, consistent with patterns observed in the field. The high-end value corresponds to a concentration of 3.2 mg/L. The linear regression relationships were evaluated and the equations were obtained using SigmaPlot ® from the natural logarithmic transformation of the paired water depth (m) and pore water sulfide (mg/L) data. Both data sets passed the normality test. The equation for F1 is:  $S = EXP(0.3507 \times depth + 2.0897)$  with S = 13, S = 13, and S = 13. The power of the performed test at a confidence level of 0.05 was poor for both relationships, with Site F1 = 0.44 and Site U3 = 0.21.

Despite the low predictive power of these equations, one can carry out the corresponding calculation of water depth equivalent to the breakpoint threshold concentration. The corresponding calculated depth at which the sulfide concentration reaches an average value of 3.2 mg/L is about 0.07 m at F1, or about 2.5 inches, and 0.16 m at U3, or about six inches. Although a rigorous uncertainty analysis has not been carried out to support this evaluation, doubling these values could provide an adequate margin of safety. Thus it is possible that maintaining an average depth of roughly one foot (0.3 m), with a minimum depth of six inches, could foster sulfide buildup where soil and surface water conditions are otherwise conducive, whether STA-2 Cell 1 is more F1-like or more U3-like in its soil chemistry and surface water-pore water interactions.

As a caveat to this approach, it is not clear that STA-2 Cell 1 is sufficiently similar to either F1 or U3 in its soil chemistry or surface water-soil chemistry interactions to warrant the use of either regression relationship. Thus the uncertainty in the results of such predictions must be considered high from a conceptual, as well as a statistical standpoint, as is the magnitude of the margin of safety required to offset that uncertainty. Therefore, it would be preferable to have supporting results from controlled field mesocosm studies of water depth-sulfide and dissolved oxygen-sulfide relationships in STA-2 Cell 1. Until such studies are carried out, only the measurement of pore water sulfide, soil and pore water methylmercury, and water depth in STA-2 Cell 1 will ensure that an average operating depth of 1 foot will foster the build-up of pore water sulfide to a concentration that strongly inhibits methylmercury production.

#### **Methylmercury Dilution**

#### **FLOW DILUTION**

All other factors being equal, the change from standing to flowing water conditions will reduce the water column concentration of methylmercury because of flow dilution. However, all other factors are not equal because the initiation of flow-through will change the relative contributions of inflow, atmospheric deposition and in situ fluxes of inorganic mercury and methylmercury and the surface water and underlying soil pore water and solids chemistries governing the transformation and transport of methylmercury. Further, higher inflow rates will generally occur in the wet season, when the wet deposition flux of inorganic mercury and peat soil temperatures are also substantially higher and inflow methylmercury concentrations are higher. Under these circumstances the combined effects of these influences on internally produced methylmercury are inherently convolved. Nevertheless, where the primary source of methylmercury is the inflow load rather than in situ production, then the interior methylmercury concentration should show strong positive correlations with external loading factors, such as the inflow rate, hydraulic loading rate and methylmercury load. Conversely, the interior methylmercury concentration should show strong negative correlations with factors related to the dilution of inflow load, such as rainfall volume and vegetation coverage, density and turnover rates. Factors relating to in situ production, such as inflow or rainfall inorganic mercury loads, water depth or hydraulic retention time, should show no, weak, or negative correlations. Where factors are mechanistically or statistically co-correlated, as in the case of flow rate and water depth, a positive correlation between water depth and the interior methylmercury concentration may be more a reflection of the relationship between inflow rate and load than between water depth, anaerobic conditions and methylmercury production. The preceding logic may explain some of the relationships observed for the ENR Project between the 13-week rolling average interior methylmercury concentration and the corresponding values for the inflow rate (r = 0.57), inflow load (r = 0.61), rain load (r = 0.30), water depth (r = -0.36), hydraulic loading rate (r = -0.19), hydraulic retention time (r = 0.06) and rainfall volume (r = 0.06) for data collected in the period 1994 through 1999 (SFWMD 1995) through 1999; unpublished District data, 1999).

#### **Biodilution**

An inverse relationship between methylmercury in fish and degree of eutrophication was observed for lakes across the United States (D'Itri et al., 1971) and Northern Europe (Hakanson, 1980). To explain this phenomenon, Hakanson (1980) speculated that the methylmercury concentration in fish was primarily controlled by three factors – pH, inorganic mercury flux and the concentration of suspended solids – and developed an empirical model that captured those influences quantitatively. Because the inorganic mercury flux is not readily measured in practice, he used the concentration of inorganic mercury in the sediments as a surrogate for this value. All three factors are influenced by the rate of primary production, and Hakanson coined the term "biodilution" to explain the apparent inverse relationship between lake productivity and methylmercury levels in fish, arguing that where the concentration of biotic particles was high, methylmercury concentrations in water, sediment and fish were low because of the enhanced rate of removal and dilution through settling and sedimentation, and vice versa. It can be predicted with high confidence that the increase in the phosphorus concentrations in, and loads to, Cell 1 following initiation of flow-through operation will increase the rate of primary production, and that this will translate into a higher peat-accretion rate (Chimney and Moustafa, 1999), higher inorganic mercury and methylmercury settling rates (Ambrose and Araujo, 1998) and a lower inorganic mercury concentration in the more rapidly accreting peat soil (SFWMD, 1995-1999), as was observed along the WCA-2A nutrient gradient (Vaithiyanathan et al., 1996).

Phosphorus has not been shown to have a direct influence on the rate of methylmercury production (Gilmour et al., 1998b). Moreover, because the soil (r = 0.70; log transformed r = 0.90), and not the water column (r = 0.55; log transformed r = 0.73), methylmercury concentration is the strongest determinant of the concentration of methylmercury in mosquitofish, and because pore water sulfide (r = -0.72; log transformed r = -0.85), and not the inorganic mercury concentration on soil solids (r = 0.66; log transformed r = 0.46), is the strongest determinant of the methylmercury concentration in soils (District analysis of USGS ACME data provided in Krabbenhoft et al., 2000), the increase in biodilution is unlikely to substantially reduce the concentrations of methylmercury in fish, which is the medium of concern from a risk-management standpoint. (Interestingly, because the direct linear correlation between pore water sulfide and mosquitofish methylmercury (r = -0.89; log transformed mosquitofish r = -0.975) is stronger than its indirect influence via the methylmercury concentration in soil, this suggests pore water sulfide is mediating methylmercury biouptake by microflora and microfauna, as well as methylmercury production, which has also been hypothesized by others, i.e., R. Mason, University of Maryland, personal communication, 2000; C. Gilmour, ANSERC, personal communication, 2001).

#### **DOWNSTREAM RECEIVING WATERS**

#### **Methylmercury Production**

#### THE EFFECT OF THE STA-2 CELL 1 INORGANIC MERCURY LOAD

As discussed in the section on "STA-2 Cell 1," following reinundation with the return of a more normal wet season, the anticipated second first-flush flux of inorganic mercury liberated from the soil is likely to be rapidly reabsorbed by the standing crop of vegetation and the surficial soil, as was the case in the first first-flush event (**Appendix 4A-6**). It is, therefore, highly unlikely that STA-2 Cell 1 will become a substantial source of excess inorganic mercury to the downstream environment following initiation of flow-through operation. The concentrations of inorganic mercury in the discharge will vary with the season, and outflow concentrations will occasionally exceed those at the inflow, as has been observed in other STAs (Rumbold et al., 1999;

2000; 2001). Overall, however, it is expected there will be net removal of inorganic mercury for the long term, due to its high affinity for accreting peat soil, as long as the soils remain inundated. This was the case in the ENR Project, which removed between 50 and 75 percent of the inorganic mercury from all sources prior to discharge (Miles and Fink, 1998; Fink, 2000).

The diversion of S-6 flow from discharge through the S-10s will reduce the inorganic mercury load to the already impacted area downstream of the S-10s, and this could have a beneficial effect on methylmercury production in the already impacted area, albeit probably only marginally. This is because the methylation rate is more strongly determined by sulfur biogeochemistry than the inorganic mercury flux or soil concentration (Gilmour et al., 1998a,b). Further, this marginal beneficial effect will decrease with downstream distance as the relative contribution of the STA-2 discharge to the inorganic mercury loading rate per unit area (flux) decreases and the relative contribution of wet and dry atmospheric deposition increases (Fink and Rawlik, 2000; C. Pollman, TetraTech, personal communication, 2001). The converse is likely to occur in the already impacted areas downstream of S-6 and S-7 for the same reasons. However, if they occur neither the marginal beneficial nor detrimental impacts of diverting S-6 flow can be attributed solely to the initiation of flow-through operation of STA-2 Cell 1.

#### The Effect of the STA-2 Cell 1 Methylmercury Load

As discussed in the section on "STA-2 Cell 1," the flux of new inorganic mercury from wet and dry atmospheric deposition, the excess inorganic mercury released from the deeper soil horizon and the inorganic mercury pulse redeposited at the soil surface are likely to support excess methylmercury production until pore water sulfide concentrations build up to inhibitory levels. However, as noted in the sections on "Factors Controlling Methylmercury Production and Bioaccumulation in and Downstream of Constructed Wetlands in the Everglades" and "STA-2 Cell 1," the *in situ* production rate of methylmercury is more strongly influenced by sulfur biogeochemistry than by the flux of labile, bioavailable inorganic mercury in runoff, wet and dry deposition or release from soil storage. This is even likely to be the case following a dryout or burn event. Krabbenhoft et al. (2001) dosed replicate mesocosms with stable mercury isotopes to trace the source of the inorganic mercury subsequently appearing as methylmercury in soil, water and mosquitofish. Even in a set of mesocosms that dried out for a period of time, the excess sulfate in reflooded soil stimulated sulfate-reducing bacteria activity, but it was the new inorganic mercury in wet and dry deposition, not the old inorganic mercury released from the soil reservoir, that was being methylated under these conditions (Krabbenhoft et al., 2001).

Following this transient excess methylmercury production event, the excess and potentially anomalously high concentrations of methylmercury likely to be present in Cell-1 discharge will be diluted with the lower concentrations from Cell 2 and Cell 3 discharges, minimizing localized adverse impacts in the immediate vicinity of the discharge. Moreover, it is unlikely that the excess methylmercury load from Cell 1 will have a substantial effect on methylmercury bioaccumulation in the already impacted areas downstream of S-6 and S-7 relative to *in situ* methylmercury production (D. Krabbenhoft, USGS-Madison, personal communication, 2001).

In the ENR Project in the period 1994 through 1999, the outflow sulfate concentration was more than 80 percent of the inflow concentration (unpublished District data, 2000), but rainfall exceeded the calculated evapotranspiration (ET) by between 10 and 15 percent (ratio of rainfall to ET in the period August 1994 through December 1998 was 1.14/1), so most of this apparent reduction could be attributed to rainfall dilution (SFWMD, 1995 through 1999). To the extent that STA-2 Cell 1 behaves like the ENR Project regarding its affinity for sulfate, STA-2 Cell 1 is expected to have a negligible effect on the sulfate loads and concentrations in the S-6 discharge.

Therefore, the rates of methylmercury production and bioaccumulation in fish in the already impacted areas downstream of S-6 and S-7 should not increase or decrease substantially as a consequence of the discharge of treated stormwater by STA-2 Cell 1. The reduction in the sulfate loading rate to the already impacted area downstream of the S-10s might increase or decrease methylmercury production and bioaccumulation there, but this will occur with the diversion of S-6 water out of the L-39 Canal and the S-10 structures and into the northern quadrant of WCA-2A, irrespective of whether flow-through operation of Cell 1 is initiated. Thus, any mercury-related effect of changes in sulfate loadings from this diversion cannot be attributed to the operation of Cell 1, *per se*.

#### **METHYLMERCURY DILUTION**

#### **Flow Dilution**

Based on the same data and reasoning as for the STA-2Cell 1 interior, it can be extrapolated with moderate confidence that the increased flow through the already impacted areas downstream of S-6 and S-7 and the decrease in the flows to the already impacted area downstream of the S-10 structures will not substantially decrease or increase, respectively, the methylmercury concentrations in water, sediment or fish in these areas. More importantly, the diversion of flow from the S-10 structures into the northern and western corners of WCA-2A will occur irrespective of the operation of STA-2 Cell 1, so any mercury related benefits or detriments resulting from that diversion cannot be attributed to the operation of STA-2 Cell 1, *per se*.

#### **Biodilution**

In a series of reports, the District evaluated the hypothesis put forth by others (PTI, 1994) that the post-STA reduction in water column phosphorus in already impacted areas of the Everglades will result in a substantial increase in methylmercury in fish due to a loss of biodilution (Fink et al., 1999; Fink and Rawlik, 2000). Based on that evaluation, the District found that:

The methylmercury production rate, not the primary production rate, was likely to be the primary determinant of the concentration of methylmercury in water, soils and fish in the already impacted areas of the Northern Everglades, and

The sulfur cycle, not the phosphorus cycle, was likely to be the primary determinant of the methylmercury production rate in the already impacted areas.

Applying these same findings to the present circumstances, the District concludes that the decrease in the water column concentrations and loads of total phosphorus to the already impacted areas downstream of S-6, S-7 and the S-10 structures will not result in a substantial increase in fish methylmercury levels or in the associated risks to fish-eating wildlife.

## MANAGEMENT OPTIONS AND THEIR ANTICIPATED ENVIRONMENTAL IMPACTS FOR ADDRESSING THE ANOMALOUS MERCURY CONDITIONS IN STA-2

Based on the above analysis, three water management options are available to the District, with potential effectiveness in moderating the rate of methylmercury production and the degree of methylmercury bioaccumulation in STA-2 Cell 1 at this time: (1) circumvent Cell 1 and operate

Cells 2 and 3 only while maintaining a water depth of at least 1 ft (0.3 m) in Cell 1 without flow-through; (2) circumvent Cell 1 and operate Cells 2 and 3 only while drying out Cell 1 by recirculating its discharge through the seepage return canal to the headwaters for discharge through Cells 2 and 3, and thence to the L-6 Canal; or (3) maintain a water depth of at least 1 ft (0.3 m) in Cell 1 while initiating flow-through operation. If the interior methylmercury concentrations remain significantly higher than those at the inflow, as is predicted, implementation of Option 3 will require a variance from the startup mercury criteria in the state permit to operate STA-2. The remainder of this section is devoted to evaluating the potential phosphorus and mercury benefits and detriments of each option.

#### **OPTION 1: STATUS QUO**

In this option, S-6 water is diverted around Cell 1 and treated by Cells 2 and 3 only. Because there can be no discharge from Cell 1 under Option 1, there can be no downstream impacts. Available water permitting, the combination of rainwater and L-4 Canal water to compensate for evapotranspiration and seepage losses (makeup water) can be held at a depth averaging 0.3 m, which, based on the analysis in the section on "The Effect of Water Depth," should ensure the rapid development of anaerobic conditions in the surficial sediment and the subsequent build-up of inhibitory concentrations of pore water sulfide, if conditions are otherwise conducive. However, the existence of anaerobic conditions in the surficial soil is necessary, but not sufficient, to ensure the accumulation of pore water sulfide to inhibitory concentrations. For example, the labile sulfur pool in Cell 1 soil, supplemented by the sulfate in makeup water, could be sufficient to stimulate the activity of sulfate-reducing bacteria, but insufficient to foster the accumulation of sulfide to inhibitory concentrations. Under such circumstances, standing water conditions during the upcoming wet season would be considered a worst case for methylmercury production, bioaccumulation and exposure for fish-eating wildlife following dryout and reflooding. The risk of chronic toxic effects to the most exposed, most sensitive members of fish-eating bird populations foraging preferentially in Cell 1 under these anomalous methylmercury conditions is likely to be unacceptably high (Appendix 4A-6). Available water permitting, it should be possible to preclude wading birds, including the endangered wood stork, from foraging in Cell 1 by holding the water at a depth of 1 m (Gawlik et al., 1999), but this would not discourage, and could encourage, foraging by diving birds, such as the anhinga, merganser and pelican. Even if methylmercury concentrations in peat soil eventually decline to levels that will no longer sustain anomalously high methylmercury concentrations at each trophic level, the amount of time it takes for the second first-flush methylmercury pulse to clear from the food chain could be years.

#### **OPTION 2: DRY-OUT CELL 1**

Option 2 can be effected by draining accumulated water out of Cell 1 and recirculating it via the discharge canal to Cells 2 and 3 for treatment prior to discharge. Subsequently, following heavy rains, this same procedure can be repeated, so Cell 1 can be kept dry for the long term. Option 2 will achieve the short-term objective of reducing or eliminating methylmercury risks to fish-eating wildlife by eliminating that pathway of exposure. However, during the drawdown, fish-eating wildlife will be attracted to STA-2 Cell 1 to feed on the fish trapped in shrinking pools, and after dryout the carrion-eating birds will feed on the remaining fish carcasses. Nevertheless, this exposure is likely to be short lived. Moreover, because there is no discharge from Cell 1 under Option 2, there can be no downstream impacts.

#### **OPTION 3: INITIATE CELL 1 FLOW-THROUGH OPERATION**

Option 3 was the operational regimen anticipated in the Programmatic Environmental Impact Statement and Federal Clean Water Act and Florida Everglades Forever Act (EFA) permit applications. If the flowing water is held at an average depth of at least 0.3 m (1 foot), with a minimum depth of 0.15 m (six inches), this is likely to cause pore water sulfide concentrations to increase to levels inhibitory of methylmercury production. Under these conditions, Option 3 is likely to achieve the short-term objective of reducing the magnitude and duration of peak methylmercury production and bioaccumulation, and the long-term objective of a lower rate of methylmercury production and bioaccumulation near steady state, with a corresponding reduction in the short- and long-term risks of methylmercury toxicity to fish-eating wildlife relative to the status quo. Because there is no drawdown, there will be no period of enhanced attractiveness to fish-eating wildlife. Because there is no dryout and rewetting, there will be no repeat of the startup "first flush" effect, except in a drought situation, which is beyond the District's control. To ensure sufficient water is available to maintain the required average and minimum water depths in STA-2 Cell 1, once it is determined that STA-2 Cell 1 capacity will be required to treat all the water from a high-flow event, flow allocation priority will be given to STA-2 Cell 1 over Cells 2 and 3. Despite these precautions, if methylmercury concentrations in fish rise to levels that have the potential to threaten public health, or endangered or migratory species, STA-2 Cell 1 can be dried out, diluting the excess methylmercury in Cell 2 and 3 discharges. In this way, any unanticipated methylmercury trajectory within STA-2 Cell 1 can be accommodated.

As to the direct downstream mercury impacts of initiating flow-through operation of Cell 1, it is reasonable to conclude that:

- 1. As with the first cycle of dryout and reflooding, the second "first-flush" inorganic mercury load will be rapidly reabsorbed in Cell 1, and any excess inorganic mercury will be diluted in the discharges from Cells 2 and 3 when flow-through operation begins;
- 2. The second "first-flush" of inorganic mercury will be transformed into a "first-flush" pulse of methylmercury, and the initially higher average methylmercury concentrations in Cell 1 discharge will be diluted by the likely lower average methylmercury concentrations in the discharges from Cells 2 and 3;
- 3. The methylmercury load from Cell 1 is not significant in terms of downstream impacts relative to the loads from Cells 2 and 3 and *in situ* methylmercury production downstream;
- 4. The load and concentration of sulfate discharged to the already impacted areas down-stream of the S-6 and S-7 Pump Stations are unlikely to change substantially with or without the use of Cell 1, so there can be no substantial effect from changes to the down-stream sulfur cycle on the downstream mercury cycle attributable to Cell 1 operation;
- 5. During high flow events, the higher hydraulic loading rates and lower hydraulic residence times in Cells 2 and 3 caused by diverting S-6 flows around Cell 1 are likely to result in a lower average total phosphorus removal efficiency by Cells 2 and 3 and a higher average total phosphorus concentration in STA-2 effluent than could be achieved if Cell 1 were online (Chimney and Moustafa, 1999); and
- 6. The decrease in the downstream total phosphorus load to the already impacted areas is likely to decrease the eutrophic conditions there (Grimshaw et al., 1993; 1997; McCormick et al., 1996; 1998; 1999), which is the primary purpose of the Everglades Forever Act, and this could eventually result in some, though not an environmentally significant,

increase in methylmercury production and bioaccumulation over the area exhibiting a decrease in the imbalance in flora and fauna (Fink et al., 1999; Fink and Rawlik, 2000).

#### CONCLUSIONS

Based on the preceding technical analysis, the District has provided substantial information to support the following conclusions:

- 1. The first first-flush release of inorganic mercury was reabsorbed by the standing crop of live, dying and dead vegetation, the biofilms living on them and the surficial soil layer, and this will also likely be the case for the second first-flush release event.
- 2. A substantial fraction of the first, first-flush inorganic mercury was transformed rapidly into methylmercury, and, this will also likely be the case for second, first flush release event.
- 3. The first methylmercury pulse was subsequently transferred to benthic organisms, their predators, and thence to the indicator organism, *Gambusia holbrookii*, the mosquitofish, and this will also likely be the case for the second methylmercury pulse.
- 4. Present levels of methylmercury in mosquitofish are indicative of a degree of contamination that represents a potentially unacceptable risk of methylmercury toxic effects for highly exposed, highly sensitive members of fish-eating populations.
- 5. Mosquitofish methylmercury concentrations are not likely to decline to levels that do not represent an unacceptable long-term risk of methylmercury toxicity to fish-eating wild-life under present circumstances and conditions.
- 6. Mercury startup criteria are not likely to be met under the combined influence of the residual inorganic mercury flux from soil release and redeposition, wet-season atmospheric deposition and status quo conditions extant in STA-2 Cell 1 over the next six months.
- 7. Initiation of flow-through operation is unlikely to increase and likely to decrease substantially the mercury risks to fish-eating wildlife in Cells 1, 2 and 3 in response to the loads or concentrations of total mercury, methylmercury and influential constituents present in the untreated inflow.
- 8. Initiation of flow-through operation per Option 3 is unlikely to increase substantially the mercury risks to fish-eating wildlife in downstream areas in response to the loads or concentrations of total mercury, methylmercury or influential constituents present in the treated outflow.
- 9. Initiation of flow-through operation is likely to increase the efficiency with which phosphorus concentrations and loads are reduced.
- 10. The foreseeable benefits of greater phosphorus load reduction under Option 3 are likely to substantially outweigh the potential detriments of possible adverse mercury impacts.
- 11. In the unlikely event the methylmercury concentrations within or downstream of STA-2 Cell 1 represent an imminent threat to the public health, safety or welfare, the District can eliminate the problem by drawing down and drying out Cell 1 and diverting S-6 flow through Cells 2 and 3 only.

These conclusions derive from a conceptual model of the mercury cycle in aquatic ecosystems developed from 25 years of general environmental mercury research, five years of Ever-

glades-specific mercury monitoring, research and modeling, and what has been learned to-date about the water chemistry in the inflow to STA-2 and the soil chemistry in STA-2 Cell 1.

Based on the technical evaluation contained in this report, the District is requesting a modification of, or variance from, the permit requirement that precludes initiation of flow-through operation until the total mercury and methylmercury concentrations in the interior of each treatment cell are not significantly greater than their corresponding inflow concentrations. This will allow the District to carry out Option 3, discussed in the preceding section. If, however, methylmercury loads, concentrations or bioaccumulations within or downstream of STA-2 increase to levels that represent an imminent threat to the public health, safety and welfare, contrary to expectations, the District can eliminate this threat by drawing down and drying out Cell 1 in a timely fashion and operating STA-2 with Cells 2 and 3 only.

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